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(54) Title: IMPROVEMENTS IN OR RELATING TO POLYMERS

(57) Abstract: Olefin homopolymers and copolymers, including novel products with essentially complete particle to particle homogeneity and having polymer chain defects introduced in a controlled manner across their molecular weight distribution, are prepared by a process comprising polymerisation under essentially constant conditions in a single reactor in the presence of a catalyst system comprising a support material coimpregnated with at least two metallocene olefin polymerisation catalysts having different propensities for incorporation of polymer chain defects.

Improvements in or relating to polymers

5 The present invention relates to a process for the
preparation of olefin polymers (including homopolymers
and copolymers), and to novel polymers obtainable
thereby. More particularly the invention relates to a
process and products wherein polymer chain defects (i.e.
10 irregularities in the otherwise regular structure of a
polymer, such as side chains or crystallinity disrupting
monomer units) are introduced in a controlled manner
across the molecular weight distribution of the polymer.

 The molecular weight distribution of polymers
15 affects their properties, in particular their mechanical
strength and processing properties. Mechanical strength
is to a large extent determined by higher molecular
weight fractions, whereas extrudability is determined by
lower molecular weight fractions. As a result,
20 polyolefins having improved mechanical and processing
properties may be obtained if the molecular weight
distribution is tailored to the end use of the polymer.
For many applications, such as extrusion and moulding
processes, polymers having a broad, or multi-modal,
25 molecular weight distribution are desirable. Polymers
having a multi-modal molecular weight distribution
consist of two or more polymer components and are
generally characterised by a broad molecular weight
distribution; such polymers exhibit excellent
30 processability.

 The mechanical properties of polymer products may
be further manipulated by the inclusion of polymer chain
defects, for example by incorporation of α -olefin
comonomers to vary the nature and relative content of
35 short chain branches present as side chains. Depending
on the nature of such a comonomer, its inclusion may
result in an increase or, less commonly, a decrease in

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the degree of branching on the main polymer backbone.

Not only the nature, but also the distribution of polymer chain defects amongst individual polymer components is important in determining polymer properties. The ability to control such distribution over the molecular weight distribution of a polymer is therefore particularly desirable, as in particular is the ability to produce multi-modal, e.g. bi-modal, molecular weight distribution copolymers in which polymer chain defects such as comonomer molecules are selectively incorporated in one part of the molecular weight distribution. Polymers having a multi-modal, e.g. bi-modal, molecular weight distribution in which such defects, in particular increased relative content of side chains resulting from comonomer inclusion, are concentrated in a higher molecular weight fraction are especially desirable. Such polymers exhibit good impact resistance, tear strength and environmental stress crack resistance. Without wishing to be bound by theory, it is believed that the presence of a polymer chain defect such as a comonomer in a higher molecular weight fraction of a polymer may stimulate formation or enhance the effect of "tie molecules" which are able to participate in more than one crystal lamella. This is believed to contribute to the improved mechanical properties, especially the improved environmental stress crack resistance, of such polymers.

In an attempt to achieve improved environmental stress crack resistance properties at corresponding melt flow rates and densities, several suggestions have been made to blend low molecular weight homopolymer and high molecular weight copolymers, for example by reactor blending using reactors in series or by blending the two separate components in an extruder (see e.g. US-A-3280220, US-A-4461873 and US-A-4547551). However, it can be difficult to mix polymers with different molecular weights to achieve a homogeneous product. In

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order to get uniform, homogeneous blends from two widely different molecular weight polymers, it is generally necessary that at least 50% by weight of the blend be of the high molecular weight component. Homogeneous blends having >50% by weight of the low molecular weight component are extremely difficult to obtain by blending methods.

Various catalyst systems have been proposed for the polymerisation of polymers and copolymers of olefins.

The preparation of broad molecular weight distribution olefin polymers in a dual reactor system using a variety of transition metal catalysts, e.g. Ziegler catalysts, is described for example in WO 92/12182. The broad molecular weight distribution results in this case from the polymerisation conditions in the different reactors favouring the production of different molecular weight polymers, e.g. one favouring the production of a higher molecular weight polymer and a second favouring production of a lower molecular weight polymer.

Broad molecular weight distribution polyolefins can be produced in a single reactor using either catalyst mixtures or multi-site catalysts, e.g. two or more metallocene complex catalysts. For example, WO 95/04761 describes the use of a combination of three metallocene complexes to produce a polymer product having a controlled molecular weight distribution. However, such a catalyst system provides for little control over levels of incorporation of polymer chain defects such as comonomer molecules.

Both conventional Ziegler-Natta catalysts and Phillips type (e.g. chromium oxide based) catalysts have been proposed for use in combination with metallocenes in the preparation of ethylene copolymers having a bimodal or otherwise broad molecular weight distribution (see e.g. EP-A-0676418, EP-A-0658571, US-A-5543376, US-A-5624877 and WO 97/27225). However, both Ziegler and

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Phillips type catalysts have a tendency to produce polymer products having an inverse dependence of molecular weight and comonomer content, i.e. the lower molecular weight polymer molecules contain a relatively higher proportion of comonomer than the higher molecular weight polymer molecules. Thus, although a degree of comonomer control is achieved, this is generally limited to incorporation of comonomer in a lower molecular weight component; by way of example the majority of the ethylene copolymers exemplified in EP-A-0676418 contain a higher proportion of copolymer in the lower molecular weight fraction, and in only one product does the comonomer level of the higher molecular weight fraction exceed that of the lower molecular weight fraction (by a factor of 2:1). As a result, such prior art products tend to exhibit a relatively poor balance of impact and stiffness and low environmental stress crack resistance.

Processes for the preparation of broad molecular weight distribution polyolefins using pairs of metallocene catalysts in conjunction with appropriate cocatalysts and support systems are described in, for example, EP-A-0619325, EP-A-0705851 and WO 98/57998. The first two of these disclosures relate to single step reactions involving the use of catalysts prepared by multistep procedures and of separate metallocene catalysts on separate supports respectively. The third relates to a multistage polymerisation process in which a low molecular weight fraction having little or no inclusion of comonomer may be produced in a first or early stage, with a bimodal high molecular weight fraction being produced with comonomer inclusion in a second or later stage.

The present invention is based on the finding that a catalyst system comprising a support material coimpregnated with at least two metallocenes and any necessary or desired cocatalyst(s) (i.e. a system in which all the catalyst and cocatalyst materials are

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simultaneously applied to the support material during preparation of the system) may be used in a single reaction stage to prepare new and useful olefin homopolymers and copolymers with highly advantageous properties. Use of metallocenes which have different propensities for incorporation of polymer chain defects permits a high degree of control over the degree of polymer chain defect incorporation into higher and lower molecular weight fractions, whilst the fact that the catalysts are coimpregnated on a single support material ensures that the polymer products have a very high degree of particle to particle homogeneity. The polymerisation process is carried out under essentially constant conditions (i.e. with temperature, pressure, comonomer and/or hydrogen concentration where appropriate, etc. not varying significantly with time) In the reactor vessel, thereby simplifying procedure and minimising operating costs. The ability to produce such intimate blends of two or more polymer components under a single set of processing conditions at different catalyst sites on a single support material is most surprising.

Thus according to one aspect of the present invention there is provided a process for the preparation of an olefin polymer wherein olefin polymerisation is effected under essentially constant conditions in a single reactor in the presence of a catalyst system comprising a support material coimpregnated with at least two metallocene olefin polymerisation catalysts having different propensities for incorporation of polymer chain defects.

It will be appreciated that the products of such a process may if desired be subjected to further polymerisation (e.g. using the above-defined method) as part of a multi-step procedure in order to prepare more complex polymers.

The metallocenes used in catalyst systems according

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to the invention are preferably selected to produce an olefin polymers in which the polymer chain defect content of a higher molecular weight fraction of the polymer is at least 3, preferably at least 5, e.g. at least 10, times that of a lower molecular weight fraction. The level of polymer chain defect incorporation in a (or the) lower molecular weight fraction of such a polymer may advantageously be zero or substantially zero, in which case this fraction may essentially constitute a homopolymer, e.g. an ethylene homopolymer. Especially preferably, the catalyst is one capable of producing a copolymer in which short chain branching derived from comonomer incorporation is mainly, e.g. exclusively, present in a higher molecular weight fraction. Incorporation of short chain branches in higher molecular weight chains is believed to enable incorporation of higher levels of comonomer into the polymer at constant density, which in turn helps to achieve a high environmental stress crack resistance.

Viewed from a further aspect the invention provides an olefin copolymer obtainable by the process in accordance with the invention, and products (e.g. containers, fibres, films, sheets, tubes, etc.) fabricated therefrom. Thus according to this aspect of the invention there is provided a polyolefin having essentially complete particle to particle homogeneity and comprising at least a higher molecular weight fraction and a lower molecular weight fraction, wherein the polymer chain defect content of said higher molecular weight fraction is at least 3 times that of said lower molecular weight fraction.

Preferred metallocenes for use in catalyst systems in accordance with the invention are those having catalytic sites capable of producing polymer components having a weight average molecular weight in the range 1,000 to 10,000,000, preferably 2,000 to 1,000,000, e.g. 2,000 to 500,000. Especially preferred catalyst systems

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are those including a first metallocene capable of producing a relatively lower weight average molecular weightMw (higher melt flow rate) polymer (e.g. having a weight average molecular weight in the range 1,000 to 1,000,000, preferably 2,000 to 500,000) with a lower level of polymer chain defect incorporation, and a second metallocene capable of producing a relatively higher weight average molecular weight (lower melt flow rate) polymer (e.g. having a weight average molecular weight in the range 10,000 to 10,000,000, preferably 50,000 to 1,000,000) with a higher level of polymer chain defect incorporation. Typical levels of polymer chain defect incorporation in a lower molecular weight component of the polymer are in the range 0 to 50, e.g. 0 to 25. Typical levels of polymer chain defect incorporation in a higher molecular weight component of the polymer will be in the range from 0.1 to about 333, e.g. 5 to 100.

As used herein, the terms "polymer chain defect level", "level of polymer chain defect incorporation" and "polymer chain defect content" are used interchangeably and are intended to define the average polymer chain defect content of any given polymer component or fraction over its entire molecular weight range. Typically, levels of polymer chain defects such as comonomers are expressed as the short chain branching frequency, i.e. the number of short chain branches per thousand carbon atoms. This may be illustrated in the case of a homopolymer of propylene, in which a single monomeric unit comprises two backbone carbon atoms and one branching methyl group, so that there is $\frac{1}{3}$ branch per total carbon atom content. This corresponds to a short chain branching frequency of $1000/3$.

However, in the case of polymers consisting mainly of branched polymer units, e.g. polypropylene, a comonomer to be incorporated may include non-branched or linear comonomers such as ethylene. Comonomers which

serve to reduce the degree of branching may act as crystallinity-disrupting units which result in a decrease in the crystallinity of the polymer material. In such cases, the comonomer level is determined by the average number of non-branched (or linear) units per thousand carbon atoms.

The process of the invention may be employed in both the homopolymerisation and copolymerisation of olefins. In the case of homopolymerisation, e.g. of ethylene, it is believed that *in situ* comonomer formation may be catalysed by one of the metallocenes, the other metallocene catalysing formation of a backbone chain with long chain branches derived from the *in situ*-generated comonomer. Such long chain branches may advantageously each contain at least 10 monomer units and may advantageously be essentially homopolymeric.

In the case of copolymerisation, at least 50% by weight of the copolymer product preferably derives from a C_{2-10} α -olefin monomer, more particularly from a C_{2-4} α -olefin monomer, preferably ethylene or propylene. The other comonomer(s) may be any monomers capable of copolymerisation with the olefin monomer, preferably mono or polyunsaturated C_{2-20} compounds, in particular monoenes or dienes, especially C_{2-10} α -olefins such as ethene, propene, but-1-ene, pent-1-ene, hex-1-ene, oct-1-ene or mixtures thereof, and may include *in situ*-generated comonomers as discussed above. Bulky comonomers, e.g. styrene or norbornene may also be used.

The process is particularly effective for the preparation of copolymers of ethene with one or more copolymerisable monomers, e.g. C_{3-20} mono and dienes, more preferably C_{3-10} α -olefin monomers, and for the preparation of copolymers of propene with one or more copolymerisable monomers, e.g. C_{4-20} mono and dienes, more preferably C_{4-10} α -olefin monomers or ethylene. The process of the invention is particularly useful for the polymerisation of ethylene and hex-1-ene.

Preferably the polymer product has ethylene as the major monomer, i.e. at least 50% by number, more preferably by weight, of the monomer residues being ethylene residues.

5 Catalyst systems containing metallocenes which respectively have stereospecific and non-stereospecific sites may also be used in accordance with the invention to produce polymers containing fractions with different crystallinities, for example polypropylenes containing
10 isotactic and atactic fractions.

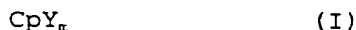
Metallocenes useful in accordance with the invention include cyclopentadienyl-containing organometallic compounds, preferably comprising a group
15 4, 5 or 6 metal, especially a group 4 metal. In cases where polymer components having different weight average molecular weights are desired, the metallocene capable of producing the lower molecular weight fraction will preferably comprise a group 4 metal.

20 Metallocenes are an example of complexes in which a metal is complexed by η -ligands, i.e. complexes in which metals are complexed by the extended Π -orbital system of organic ligands. In the present invention metal: η -ligand complexes may be used where the metal is
25 complexed by one, two or more η -ligands. The use of twin η -ligand metallocenes and single η -ligand "half metallocenes" (e.g. those developed by Dow) is particularly preferred. However, the term metallocene as used herein is used to refer to all such
30 catalytically active complexes containing one or more η -ligands. The metal in such complexes is preferably a group 4, 5, 6, 7 or 8 metal or a lanthanide or actinide, especially a group 4, 5 or 6 metal, particularly Zr, Hf, Ti or Cr. The η -ligand preferably comprises a
35 cyclopentadienyl ring, optionally with a ring carbon replaced by a heteroatom (e.g. N, B, S or P), optionally substituted by pendant or fused ring substituents and optionally linked by a bridge (e.g. a 1 to 4 atom bridge

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such as $(\text{CH}_2)_2$, $\text{C}(\text{CH}_3)_2$ or $\text{Si}(\text{CH}_3)_2$ to a further optionally substituted homo or heterocyclic cyclopentadienyl ring. The ring substituents may for example be halo atoms or alkyl groups optionally with
5 carbons replaced by heteroatoms such as O, N and Si, especially Si and O and optionally substituted by mono or polycyclic groups such as phenyl or naphthyl groups. Examples of such homo or heterocyclic cyclopentadienyl ligands are well known from the scientific and patent
10 literature, e.g. from the published patent applications of Hoechst, Montell, Borealis, Exxon, and Dow, for example EP-A-416815, WO 96/04290, EP-A-485821, EP-A-485823, US-A-5276208 and US-A-5145819.

Thus the η -bonding ligand may for example be of
15 formula I



where Cp is an unsubstituted, mono-substituted or polysubstituted homo or heterocyclic cyclopentadienyl,
20 indenyl, tetrahydroindenyl, fluorenyl, benzindenyl, cyclopenta[1]phenanthrenyl, azulenyl, or octahydrofluorenyl ligand; m is zero or an integer having a value of 1, 2, 3, 4 or 5; and where present each Y which may be the same or different is a
25 substituent attached to the cyclopentadienyl ring moiety of Cp and selected from halogen atoms, and alkyl, alkenyl, aryl, aralkyl, alkoxy, alkylthio, alkylamino, $(\text{alkyl})_2\text{P}$, alkylsilyloxy, alkylgermyloxy, acyl, acyloxy and amido groups or one Y comprises an atom or group
30 providing an atom chain comprising 1 to 4 atoms selected from C, O, S, N, Si and P, especially C and Si (e.g. an ethylene group) to a second unsubstituted, mono-substituted or polysubstituted homo or heterocyclic cyclopentadienyl, indenyl, tetrahydroindenyl, fluorenyl
35 or octahydrofluorenyl ligand group.

In the η -bonding ligands of formula I, the rings fused to the homo or hetero cyclopentadienyl rings may

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themselves be optionally substituted e.g. by halogen atoms or groups containing 1 to 10 carbon atoms.

Many examples of such η -bonding ligands and their synthesis are known from the literature, see for example: Möhring et al. J. Organomet. Chem 479:1-29 (1994), Brintzinger et al. Angew. Chem. Int. Ed. Engl. 34:1143-1170 (1995).

Examples of suitable η -bonding ligands include the following:

10 cyclopentadienyl, indenyl, fluorenyl, pentamethyl-cyclopentadienyl, methyl-cyclopentadienyl, 1,3-dimethyl-cyclopentadienyl, i-propyl-cyclopentadienyl, 1,3-di-i-propyl-cyclopentadienyl, n-butyl-cyclopentadienyl, 1,3-di-n-butyl-cyclopentadienyl, t-butyl-cyclopentadienyl, 1,3-di-t-butyl-cyclopentadienyl, trimethylsilyl-cyclopentadienyl, 1,3-di-trimethylsilyl-cyclopentadienyl, benzyl-cyclopentadienyl, 1,3-dibenzyl-cyclopentadienyl, phenyl-cyclopentadienyl, 1,3-di-phenyl-cyclopentadienyl, naphthyl-cyclopentadienyl, 20 1,3-di-naphthyl-cyclopentadienyl, 1-methyl-indenyl, 1,3,4-trimethyl-cyclopentadienyl, 1-i-propyl-indenyl, 1,3,4-tri-i-propyl-cyclopentadienyl, 1-n-butyl-indenyl, 1,3,4-tri-n-butyl-cyclopentadienyl, 1-t-butyl-indenyl, 1,3,4-tri-t-butyl-cyclopentadienyl, 1-trimethylsilyl-indenyl, 1,3,4-tri-trimethylsilyl-cyclopentadienyl, 1-benzyl-indenyl, 1,3,4-tri-benzyl-cyclopentadienyl, 1-phenyl-indenyl, 1,3,4-tri-phenyl-cyclopentadienyl, 1-naphthyl-indenyl, 1,3,4-tri-naphthyl-cyclopentadienyl, 1,4-dimethyl-indenyl, 1,4-di-i-propyl-indenyl, 1,4-di-n-butyl-indenyl, 1,4-di-t-butyl-indenyl, 1,4-di-trimethylsilyl-indenyl, 1,4-di-benzyl-indenyl, 1,4-di-phenyl-indenyl, 1,4-di-naphthyl-indenyl, methyl-fluorenyl, i-propyl-fluorenyl, n-butyl-fluorenyl, t-butyl-fluorenyl, trimethylsilyl-fluorenyl, benzyl-fluorenyl, phenyl-fluorenyl, naphthyl-fluorenyl, 5,8-dimethyl-fluorenyl, 5,8-di-i-propyl-fluorenyl, 5,8-di-n-butyl-fluorenyl, 5,8-di-t-butyl-fluorenyl, 5,8-di-

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trimethylsilyl-fluorenyl, 5,8-di-benzyl-fluorenyl, 5,8-di-phenyl-fluorenyl and 5,8-di-naphthyl-fluorenyl.

Besides the η -ligand, the catalyst complex used according to the invention may include other ligands; typically these may be halide, hydride, alkyl, aryl, alkoxy, aryloxy, amide, carbamide or other two electron donor groups.

In a preferred embodiment the catalyst composition comprises two η -ligand catalysts, preferably a combination of unbridged and bridged bis- η -liganded complexes of group 4, 5 or 6 metals, e.g. where the unbridged η -ligand complex is a metallocene with two homo or heterocyclopentadienyl ligands which are optionally ring substituted by fused or pendant substituent groups and the bridged η -ligand complex comprises two η -liganding groups joined by a 1 to 4 atom chain. One example of a metallocene combination would thus be (i) an unbridged biscyclopentadienyl Ti, Zr or Hf compound and (ii) a bridged bis-indenyl Ti, Zr or Hf compound, e.g. substituted Cp_2ZrCl_2 in combination with optionally substituted $\text{CH}_2\text{CH}_2(\text{Ind})_2\text{ZrCl}_2$ or $\text{Si}(\text{CH}_3)_2(\text{Ind})_2\text{ZrCl}_2$. An alternative combination would be a dimethylsilylbis(fluorenyl) Ti, Zr or Hf complex (e.g. optionally substituted $\text{SiMe}_2(\text{fluorenyl})\text{ZrCl}_2$) and a substituted biscyclopentadienyl Ti, Zr or Hf complex. Particularly preferred catalyst combinations for use in the invention include (i) $\text{Cp}^*_2\text{ZrCl}_2$ (Cp^* = pentamethyl substituted cyclopentadienyl) and rac-dimethyl silylbis(2-methyl-4-phenyl)indenyl zirconium dichloride; (ii) $\text{Cp}^*_2\text{ZrCl}_2$ and bis(n-butylcyclopentadienyl) hafnium dichloride; and (iii) $(\text{nBuCp})_2\text{ZrCl}_2$ and $\text{Et}(1\text{-Ind})_2\text{HfCl}_2$.

The different types of catalyst sites in the catalyst material used in the process of the invention may be present in substantially equal numbers (i.e. a mole ratio of 1:1, or 1:1:1, etc. for two or three catalyst-type systems). However one catalyst type may be predominant with other catalyst types being present

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at a relative mol. % of for example 1 to 100% (100% representing a 1:1 mole ratio), preferably 5 to 80%, especially 10 to 70%.

5 For use in olefin polymerisation, the catalyst system may include one or more cocatalysts or catalyst activators and in this regard any appropriate cocatalyst or activator may be used.

10 Examples of cocatalysts and catalyst activators suitable for use in the invention include aluminium trialkyls (e.g. triethylaluminium), aluminoxanes such as methylaluminoxane, cationic activators such as boron containing compounds, transition metal compounds (e.g. halogenide compounds), magnesium compounds, group 3 organometallic compounds, e.g. aluminium or boron based
15 compounds. Such materials may be solids, liquids or may be in solution in a liquid phase of the catalyst material which may be a solution, a solid, a dispersion, a suspension, a slurry, etc.

20 Preferred aluminoxanes include C_{1-10} alkyl aluminoxanes, in particular methyl aluminoxane and aluminoxanes in which the alkyl groups comprise isobutyl groups optionally together with methyl groups. Such aluminoxanes may be used as the sole cocatalyst or alternatively may be used together with other
25 cocatalysts. Thus besides or in addition to aluminoxanes other cation complex forming catalyst activators may be used. In this regard mention may be made of the silver and boron compounds known in the art. What is required of such activators is that they should
30 react with the η -liganded complex to yield an organometallic cation and a non-coordinating anion (see for example the discussion on non-coordinating anions J in EP-A-617052 (Asahi)).

35 Aluminoxane cocatalysts are described by Hoechst in WO 94/28034. These are cyclic oligomers of cage-like structure having up to 40, preferably 3 to 20, $\{Al(R'')O\}$ repeat units (where R'' is hydrogen, C_{1-10} alkyl

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(preferably methyl and/or isobutyl) or C₆₋₁₈ aryl or mixtures thereof).

The support material of the catalyst system may be an inorganic or organic carrier material, preferably a solid particulate material which is preferably porous. Conventional catalyst support materials may be used in this regard, e.g. porous inorganic or organic materials, for example oxides such as silica, alumina, silica-alumina, silica with Ti, zirconia, etc, non-oxides such as magnesium halides, e.g. MgCl₂, aluminium phosphate, zeolites etc, and polymers such as polystyrene, polymethacrylate, polystyrene-divinylbenzene and polyolefins such as polyethylene and polypropylene.

Where an inorganic support material is used, this will preferably be treated, e.g. thermally or chemically to remove surface hydroxyl.

It is preferred that the ratio between the different metallocenes be substantially uniform within carrier particles, i.e. it is preferred that the ratio be the same on the surface as it is at different depths within the particles and that the ratio be substantially uniform between the particles.

The polymerisation may be effected using conventional procedures, e.g. as a slurry, gas phase, solution or high pressure polymerisation. Slurry polymerisation includes polymerisation at slightly supercritical conditions. Mixed gas phase and slurry reactors are preferred. Slurry polymerisation (e.g. bulk polymerisation) is preferably effected, e.g. in a tank reactor or more preferably a loop reactor. In slurry reactors, if a major monomer is propylene this may also function as a solvent/diluent as well as a reagent. If the major monomer is ethylene, a non-polymerizable organic compound, e.g. a C₃₋₁₀ alkane, for example propane or isobutane, may be used as a diluent. Where this is done, the volatile non-reacted or non-reactive materials will desirably be recovered and

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reused.

The reactor used in the process of the invention may conveniently be any of the conventionally used polymerisation reactors, e.g. reactors for solution
5 polymerisation, slurry tank or slurry loop polymerisation or gas phase polymerisation, etc.

For slurry reactors, the reaction temperature will generally be in the range 60 to 110°C (e.g. 85-110°C), the reactor pressure will generally be in the range 5 to
10 80 bar (e.g. 25-65 bar), and the residence time will generally be in the range 0.3 to 5 hours (e.g. 0.5 to 2 hours). The diluent used will generally be an aliphatic hydrocarbon having a boiling point in the range -70 to +100°C. In such reactors, polymerisation may if desired
15 be effected under supercritical conditions, especially in loop reactors.

For gas phase reactors, the reaction temperature used will generally be in the range 60 to 115°C (e.g. 70 to 110°C), the reactor pressure will generally be in the
20 range 10 to 25 bar, and the residence time will generally be 1 to 8 hours. The gas used will commonly be a non-reactive gas such as nitrogen together with monomer (e.g. ethylene or propylene).

For solution phase reactors, the reaction
25 temperature used will generally be in the range 130 to 270°C, the reactor pressure will generally be in the range 20 to 400 bar and the residence time will generally be in the range 0.1 to 1 hour. The solvent used will commonly be a hydrocarbon with a boiling point
30 in the range 80-200°C.

The catalyst material is introduced into the reactor used in the process of the invention as a single material containing all the components of the catalyst material, and may be a solution, a solid, a dispersion,
35 a suspension or a slurry, etc.

Generally the quantity of catalyst used will depend upon the nature of the catalyst, the reactor types and

- 16 -

conditions and the properties desired for the polymer product. Conventional catalyst quantities, such as described in the publications referred to herein, may be used.

5 In the process of the invention, hydrogen may be used to further control the molecular weight of the olefin copolymer produced in the reactor. Molecular weight control may be effected through control of the hydrogen concentration or, alternatively, through
10 control of the hydrogen consumption during the polymerisation process. In such cases, it is preferable to use a catalyst system which is responsive to hydrogen. Control over the molecular weight of the polymer can be readily achieved by monitoring the
15 hydrogen and monomer consumption, i.e. for hydrogen the difference between hydrogen input and hydrogen output and for monomer the difference between monomer input and output. The ratio of hydrogen consumption to monomer consumption can be correlated well with polymer
20 molecular weight and the product molecular weight can accordingly be adjusted to the desired level using this correlation and by appropriate adjustment of the hydrogen and monomer feed rate levels.

 The process of the invention may optionally
25 comprise further stages in addition to that of polymerisation, e.g. drying steps; blending of the polymer product with one or more further materials, e.g. further polymers, antioxidants, radiation (e.g. UV-light) stabilizers, antistatic agents, fillers,
30 plasticisers, carbon black, colours, etc.; granulation, extrusion and pelletization; etc.

 The final polymer products of the process of the invention preferably have a melt flow rate of 0.1 to 500, a weight average molecular weight of 30,000 to
35 500,000 and a melting point of 70-165°C (e.g. 70-136°C for copolymers of ethylene and 120 to 165°C for copolymers of propylene).

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Such polymers may be formulated together with conventional additives, e.g. antioxidants, UV-stabilizers, colours, fillers, plasticisers, etc. and may be used for fibre or film extrusion, for raffia, for pipes, for cable or wire applications or for moulding, e.g. injection moulding, blow moulding, rotational moulding, etc., using conventional moulding and extrusion equipment.

The products of the invention have improved molecular weight and polymer chain defect distributions. The process of the invention may be used with particular advantage to tailor the distribution of molecular weights in the higher molecular weight fraction of the overall polymer and this may be done in such a way as to include comonomer (which may provide side chains and as a result increased strength) primarily in the high molecular weight fraction. For example, using the process of the invention, comonomer may incorporate more into the longer rather than the shorter polymer chains as compared, for example, with the product obtained using a Ziegler or Phillips type catalyst in a similar process, so improving the mechanical properties of the polymer product. The presence of a bi-modal or multi-modal distribution at the higher end of the molecular weights which may be achieved using appropriate metallocene combinations improves ease of homogenisation, as the lower molecular weight component of the high molecular weight fraction reduces viscosity of the high molecular weight fraction. Without this lower end to it the higher molecular weight fraction may give rise to melt homogenization problems, thereby resulting in an inhomogeneous melt.

Thus the process of the invention allows the user to tailor the placement of comonomer into a high molecular weight fraction of a polymer and also to tailor the molecular weight profile of such a higher molecular weight fraction of a polymer.

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The polymers produced using the catalysts or processes according to the invention have a number of beneficial properties relative to polymers produced using conventional techniques. For example, where a
5 comonomer such as but-1-ene or hex-1-ene is used, this incorporates primarily into the longer rather than the shorter polymer chains so improving the mechanical and processing properties of the polymer product.

Furthermore, the polymer products have a high
10 degree of particle to particle homogeneity. The homogeneity of a polymer is often a matter of particular concern to end users since inhomogeneity may give rise to phenomena known as fish eyes, gels or white spots. This is particularly important for films but is also
15 important for wires, cables, blow moulded products, injection moulded products, rotational moulded products, pipes and fibres.

The production of highly homogeneous multi-modal, e.g. bi-modal, olefin polymers having controlled
20 comonomer incorporation in a single polymerisation stage has up to now been problematical. The use of simultaneous coimpregnation of catalyst support particles in the process of the invention to produce supported catalysts having two or more catalytic sites
25 with different comonomer propensities results in supported catalysts which can be used to produce highly homogeneous polymers in a single stage polymerisation, in a far more simple manner than has hitherto been thought possible.

30 The polymers produced in accordance with the process of the invention may be analysed by techniques well known in the art. Techniques suitable for isolating individual fractions of a sample of the copolymer include temperature rising elution
35 fractionation. Differential scanning calorimetry, preferably using a stepwise isothermal segregation technique, may be used to measure comonomer content (see

- 19 -

J.A. Parker, D.C. Bassett, R.H. Olley & P. Jääskeläinen, *Polymer* 35 [1994], 4140). There are several methods known in the art for determining the molecular weight distribution of a particular polymer sample; typically
5 it may be determined by gel permeation chromatography.

The contents of all of the documents referred to above are hereby incorporated herein by reference.

The invention will now be described further with reference to the following non-limiting Examples and the
10 attached Figures in which:

Figure 1 shows differential scanning calorimetry curves for polymers produced using conventional single site catalyst systems;

15 Figures 2-5 and 7 show differential scanning calorimetry curves for polymers in accordance with the invention produced using dual site catalyst systems and corresponding differential scanning calorimetry curves for polymers produced using conventional single site catalyst systems;

20 Figure 6 shows a gel permeation chromatography curve for a polymer produced in accordance with the invention and corresponding gel permeation chromatography curves for polymers produced using conventional single site catalyst systems.

25 Figure 8 shows gel permeation chromatography curves for ethylene homopolymers produced in accordance with the invention.

In the following Examples, the following abbreviations are used:

30

Cp* = pentamethyl-substituted cyclopentadienyl ligand, $(CH_3)_5Cp$;

GPC = gel permeation chromatography;

35

MAO - methyl aluminoxane;

- 20 -

MW = molecular weight

Mw = weight average molecular weight;

5 MWD = molecular weight distribution;

SIST = stepwise isothermal segregation technique;

TREF = temperature rising elution fractionation.

10

Example 1 - Preparation of Catalysts

Supported Catalyst (A)

15 A catalyst solution was prepared by mixing the following chemicals:

- 0.0024 g rac-dimethylsilyl bis(2-methyl-4-phenylindenyl)zirconium dichloride
- 20 - 2.2 ml MAO solution (30 wt% MAO in toluene)
- 1 ml toluene.

The resulting solution was stirred for 30 minutes at ambient temperature.

25

The solution was then added dropwise with stirring to 2 g of 55SJ, a porous particulate silica supplied by Grace company. The silica had been previously calcined in a flow of dry air at 600°C. The catalyst solution
30 was added dropwise in a ratio of 2 g carrier to 3.2 ml catalyst solution. Stirring was continued for a further 60 minutes at ambient temperature. Over a period of 60 minutes, the mixture was dried by nitrogen flow to yield a supported catalyst.

35

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Supported Catalyst (B)

A catalyst solution was prepared by mixing the following chemicals:

5

- 0.0248 g Cp*₂ZrCl₂
- 2.2 ml MAO solution (30 wt% MAO in toluene)
- 1 ml toluene.

10 The resulting solution was stirred for 30 minutes at ambient temperature.

The solution was then added dropwise with stirring to 2 g of 55SJ as described above. Stirring was continued
15 for a further 60 minutes at ambient temperature. Over a period of 90 minutes, the mixture was dried by nitrogen flow to yield a supported catalyst.

Supported Catalyst (C)

20

A catalyst solution was prepared by mixing the following chemicals:

- 0.0248 g Cp*₂ZrCl₂
- 25 - 0.0028 g rac-dimethylsilyl bis(2-methyl-4-phenylindenyl)zirconium dichloride
- 2.2 ml MAO solution (30 wt% MAO in toluene)
- 1 ml toluene.

30 The resulting solution was stirred for 30 minutes at ambient temperature.

The solution was then added dropwise with stirring to 2 g of 55SJ as described above. Stirring was continued
35 for a further 60 minutes at ambient temperature. Over a period of 90 minutes, the mixture was dried by nitrogen flow to yield a supported catalyst.

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Supported Catalyst (D)

A catalyst solution was prepared by mixing the following chemicals:

5

- 0.002 g bis(n-butylcyclopentadienyl)hafnium dichloride
- 2.2 ml MAO solution (30 wt% MAO in toluene)
- 1 ml toluene.

10

The resulting solution was stirred for 30 minutes at ambient temperature.

The solution was then added dropwise with stirring to 2 g of 55SJ as described above. Stirring was continued for a further 60 minutes at ambient temperature. Over a period of 120 minutes, the mixture was dried by nitrogen flow to yield a supported catalyst.

20 **Supported Catalyst (E)**

A catalyst solution was prepared by mixing the following chemicals:

25

- 0.0244 g $Cp^*_2ZrCl_2$
- 0.002 g bis(n-butylcyclopentadienyl)hafnium dichloride
- 2.2 ml MAO solution (30 wt% MAO in toluene)
- 1 ml toluene.

30

The resulting solution was stirred for 30 minutes at ambient temperature.

The solution was then added dropwise with stirring to 35 2 g of 55SJ as described above. Stirring was continued for a further 60 minutes at ambient temperature. Over a period of 120 minutes, the mixture was dried by nitrogen

- 23 -

flow to yield a supported catalyst.

Example 2 - Polymerisation

- 5 Ethylene polymerisation using catalysts (A) to (E) was carried out in a 2 litre reactor. Isobutane (1 litre) containing 0.02 wt% hexene and the catalyst was charged into the reactor and the temperature and pressure brought up to the desired levels.
- 10 Pure ethylene gas was added through a pressure control valve and polymerisation carried out under the following conditions: total pressure = 24 bars, temperature = 80°C and polymerisation time = 60 minutes.
- 15 The results are set out in Table 1 below.

Table 1

	Catalyst (A)	Catalyst (B)	Catalyst (C)	Catalyst (D)	Catalyst (E)
Catalyst weight (g)	0.424	0.31	0.331	0.478	0.417
Ethylene partial press. (bar)	10	10	10	10	10
C ₄ /Ethylene Cascade (wt.% C ₄)	5	5	5	5	5
Polymer weight (g)	177	41	34	235	70
Productivity (g polymer/g catalyst)	417	132	103	492	168
Activity (g/g.h)	1,565	132	103	492	168
GPC, Mw	710,000	345,000	255,000	570,000	405,000
GPC, Mn	150,000	53,000	60,000	165,000	80,000
GPC, MWD	4.7	6.5	4.3	3.5	5.1
Remarks	Fouling			Fouling	

- 25 -

DSC analyses with SIST annealing were carried out under the following conditions:

5	Step	Temperature (°C)	Time at temperature (mins)	Rate to next temperature (K/min)
	1	200	5	200
10	2	131	120	200
	3	118	120	200
	4	105	120	200
	5	92	120	200
	6	79	120	200
15	7	66	120	1
	8	10		

Each sample was then heated at a rate of 10K/min to produce the melting curves given in attached Figures 1 to 5.

Figure 1 shows melting curves for the polymers produced using catalysts (A) and (D). The same height of curve at different melting temperatures is indicative of a greater proportion of the polymer at the lower melting temperature than at the higher. This is due to the difference in crystallinity and hence lower specific melting enthalpy at lower melting temperatures. The height of the curves in Figure 1 therefore indicates the relative concentration of the polymer at each melting temperature. This means that the product produced using catalyst (A) has lower crystallinity than that produced using catalyst (D), and the cross-over point is about 65°C. Both of these polymers were found to exhibit a degree of fouling in the reactor.

Figures 2 and 3 show melting curves for the polymer

- 26 -

produced using the dual site catalyst (E) and for the polymers produced using the corresponding single site catalysts, (B) and (D). The dual site catalyst did not exhibit fouling. This is considered surprising given
5 that the low crystallinity polymer components each have melting temperatures lower than the polymerisation temperature. The dual site DSC curves correspond to a product having low crystallinity components and correspond well with the melting curves for those
10 products produced from the individual catalyst components. The shift of the main peak may be explained by co-crystallisation.

Figures 4 and 5 show melting curves for the polymer
15 produced using the dual site catalyst (C) and for the polymers produced using the corresponding single site catalysts, (A) and (B). The dual site catalyst did not exhibit fouling.

20 In Figures 1 to 5, the numbers appearing above the temperature scale represent the % by weight (calculated) of hexene corresponding to that melting temperature. These numbers have been calculated from a calibration based on single site polyethylenes and fractions
25 collected after fractionation according to chemical structure. The calibration was made by a linear approximation of co-monomer content (as determined by C-13 NMR) and melting temperature (as determined by DSC) according to the following equation:

30

$$Y = -0.5228.t + 68.205$$

where Y is wt.% hexene and t is the melting temperature. Similarly, comonomer content may be determined according
35 to the equation:

$$Y = -0.8714.t + 113.67$$

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where Y is comonomer content (branches per 1000 C atoms)
and t is the melting temperature.

5 GPC analyses were carried out under the following
conditions:

Equipment: Waters 150CV plus no. 1115
Detector: Refractive Index (RI) and Viscosity
detector
10 Calibration: Narrow Molecular weight distribution PS
(1115-9903)
Columns: 3 x HT6E styragel from Waters (140°C)

15 Results are given in attached Figure 6. The high
molecular weight tail for the polymer produced using
catalyst (E), marked (*) is to be noted. This is
considered to be higher than would be expected from a
simple summation of molecular weights and may be
evidence of a general synergistic effect of the dual
20 site catalyst systems in accordance with the invention.

The low crystallinity/high comonomer/high Mw tail
profile confirms that a product comprising a mixture of
low and high molecular weight, homo and copolymers, may
25 be produced in accordance with the invention in a single
reaction stage.

Example 3 - Catalyst Preparation

30 Supported Catalyst (F)

The catalyst was produced analogously to supported
catalyst (D) except that zirconium was used in place of
hafnium and the relative amounts were adjusted to
35 produce a supported catalyst product comprising
0.027 mmol (nBuCp)₂ZrCl₂/g carrier; and 5.6 mmol Al (from
MAO)/g carrier.

Supported Catalyst (G)

A dually impregnated carrier was prepared as above using a catalyst solution prepared by mixing 0.044 g
 5 (nBuCp)₂ZrCl₂, 0.0269 g Et(1-Ind)₂HfCl₂, 1.2 ml MAO solution (30 wt% MAO in toluene from Albemarle SA), and 0.4 ml toluene.

By calculation the supported catalyst product comprised
 10 0.011 mmol (nBuCp)₂ZrCl₂/g carrier; 0.0531 mmol Et(1-Ind)₂HfCl₂/g carrier; and 5.5 mmol Al (from MAO)/g carrier.

Example 4 - Polymerisation

15 Ethylene polymerisation using catalysts (F) and (G) was carried out in a 2 litre semi-batch reactor (continuous feeding of ethylene). Isobutane (1 litre) containing hexene and the catalyst was charged into the reactor and
 20 the temperature and pressure brought up to the desired levels (85°C and 29 bar). Polymerisation was effected for 60 minutes in the absence of hydrogen.

Results are set out in Table 2 below:

25

Table 2

	Catalyst (F)	Catalyst (G)	Catalyst (G)
30 Hexene (wt% in isobutane)	2.9	2.9	0.18
Mw (g/mol)	105,000	130,000	175,000
MWD	2.1	2.4	2.7
Tm (peak) (°C)	122.6	125.2	132.2
ΔH _m	148.0	147.5	181.8
35 Activity	6,692	1,533	737

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DSC curves for the final polymer products are shown in attached Figure 7. These DSC measurements have been obtained with standard annealing, i.e. crystallisation from 200°C to 0°C with a cooling rate of 10K/min, and melting as for the SIST method.

The polymer made with catalyst (F) with a high hexene concentration during polymerisation shows a typical single component co-polymer DSC melting behaviour.

10

The polymers made with catalyst (G) each contain two components of different crystallinity. This is most obvious on the product made with a high hexene concentration where a clear shoulder in the high crystallinity area is seen. The total curve is also shifted towards higher melting temperatures. This may be due to the high comonomer response from the Hf sites which consume most of the added comonomer, thereby causing a lower incorporation of comonomer in the polymer produced by the Zr sites. For the product made with a low hexene concentration, a disturbance on both sides of the peak can be detected, indicating at least two components.

The product made with catalyst (G) with a high hexene concentration during polymerisation has a higher Mw and Molecular weight distribution than that made with catalyst (F). This, together with an increase in melting temperature, and maintained melting enthalpy, is explained by the presence of two polymer fractions, one with a lower Mw and comonomer content than the other.

Example 5 - Polymerisation

Ethylene homopolymerisations using catalysts (C) and (E) were carried out in a 2 litre reactor. Dry catalyst was introduced into the reactor under nitrogen purging,

- 30 -

whereafter hexene-free isobutane (650 ml) was added and the temperature was rapidly raised from 15 to 80°C. Pure ethylene gas was added to raise the ethylene partial pressure from 0 to 10 bar over 2 minutes, giving a total reactor pressure of 24 bar. The polymerisation time was 60 minutes. Results are shown in the following Table 3:

Table 3

10

	Catalyst (C)	Catalyst (E)
Catalyst weight (mg)	420	320
Polymer weight (g)	4	3
GPC Mw	1,000,000	600,000
GPC Mn	40,000	38,000
weight averaged g'	0.7	0.8

15

[g' is the ratio of measured viscosity to the theoretical viscosity of linear polymer with the same molecular weight]

20

Measurements of viscosity against molecular weight confirmed that the samples exhibited viscosity properties intermediate between those of a linear polyethylene (g' = 0.95) and a highly branched polyethylene (HPPE with g' = 0.61).

25

Figure 8 shows the MWD of the samples from GPC measurements, the abscissa showing log (MW) and the ordinate showing $dW.MW/d(MW)$ where W is the mass or mass fraction of polymer.

30

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Example 6 - Catalyst preparations**Supported Catalyst (H)**

5 The catalyst was prepared analogously to supported catalyst (F) to give a supported catalyst product comprising 0.0314 g rac-dimethylsilyl bis(indenyl)-zirconium chloride.

10 **Supported Catalyst (I)**

The catalyst was prepared analogously to supported catalyst (F) to give a supported catalyst product comprising 0.0384 g dimethylsilyl bis(9-fluorenyl)-zirconium chloride.

Supported Catalyst (J)

20 A dually impregnated carrier was prepared analogously to supported catalyst (G) to give a supported catalyst comprising 90 mol% (0.0283 g) of rac-dimethylsilyl bis(indenyl)zirconium chloride and 10 mol% (0.0038 g) of dimethylsilyl bis(9-fluorenyl)zirconium chloride.

25 Example 7 - Polymerisation

Propylene polymerisations using catalysts (H) - (J) were carried out in a 2 litre reactor. Dry catalyst was introduced into the reactor under nitrogen purging, whereafter polypropylene (650 ml) was added. After 8 minutes prepolymerisation at 15°C the temperature was rapidly raised to 70°C. The polymerisation time was 60 minutes. Results are shown in the following Table 4:

35

Table 4

	Catalyst (H)	Catalyst (I)	Catalyst (J)
Mw	40,000	200,000	42,000
Mn	20,000	60,000	15,000
MWD	2	3.3	2.8
Crystallinity	high	very low	mixed

5
10 11% of the polymer produced using catalyst (J) was xylene soluble, this fraction having Mw 120,000 and Mn 6,000 (MWD = 20), whereas the xylene insoluble crystalline phase had Mw 37,000 and Mn 19,000 (MWD = 2). This confirms the presence of both high crystalline and low crystalline fractions within this bimodal product.

Claims:

1. A process for the preparation of an olefin polymer which comprises effecting olefin polymerisation under essentially constant conditions in a single reactor in the presence of a catalyst system comprising a support material coimpregnated with at least two metallocene olefin polymerisation catalysts having different propensities for incorporation of polymer chain defects.
2. A process as claimed in claim 1 wherein said metallocenes are selected to produce an olefin polymer comprising at least a higher molecular weight fraction and a lower molecular weight fraction, wherein the polymer chain defect content of said higher molecular weight fraction is at least 3 times that of said lower molecular weight fraction.
3. A process as claimed in claim 2 wherein said metallocenes are selected so that the polymer chain defect content of said higher molecular weight fraction is at least 10 times that of said lower molecular weight fraction.
4. A process as claimed in any preceding claim wherein at least one of said metallocenes comprises a group 4 metal.
5. A process as claimed in claim 4 wherein the catalyst system comprises at least a first metallocene selected from rac-dimethylsilyl bis(2-methyl-4-phenylindenyl)zirconium dichloride, bis(n-butylcyclopentadienyl)hafnium dichloride, ethyl bis(1-indenyl)hafnium dichloride and rac-dimethylsilyl bis(9-fluorenyl)zirconium dichloride and a second metallocene selected from bis(pentamethylcyclopentadienyl)zirconium dichloride, bis(n-butylcyclopentadienyl)zirconium

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dichloride and dimethylsilyl bis(9-fluorenyl)zirconium dichloride.

6. A process as claimed in any preceding claim wherein
5 the catalyst system further comprises a cocatalyst.
7. A process as claimed in claim 6 wherein said
cocatalyst is methyl aluminoxane.
- 10 8. A process as claimed in any preceding claim wherein
the support material is porous particulate silica.
9. A process as claimed in any preceding claim wherein
ethylene or propylene is polymerised.
15
10. A process as claimed in claim 9 wherein
polymerisation is effected in the presence of an α -
olefin comonomer containing up to 10 carbon atoms.
- 20 11. A process as claimed in claim 10 wherein ethylene
is copolymerised with 1-hexene.
12. A process as claimed in any preceding claim wherein
the olefin polymer is subsequently subjected to at least
25 one further polymerisation reaction.
13. A process as claimed in claim 12 wherein said
further polymerisation reaction comprises a process as
defined in claim 1.
30
14. A polyolefin having essentially complete particle
to particle homogeneity and comprising at least a higher
molecular weight fraction and a lower molecular weight
fraction, wherein the polymer chain defect content of
35 said higher molecular weight fraction is at least 3
times that of said lower molecular weight fraction.

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15. A polyolefin as claimed in claim 14 wherein the polymer chain defect content of said higher molecular weight fraction is at least 10 times that of said lower molecular weight fraction.
- 5
16. A polyolefin as claimed in claim 14 or claim 15 wherein the polymer chain defects are selected from side chains and crystallinity disrupting monomer units.
- 10
17. A polyolefin as claimed in claim 16 wherein the polymer chain defects comprise comonomer-derived short chain branches.
- 15
18. A polyolefin as claimed in claim 16 or claim 17 wherein the polymer chain defects comprise long chain branches containing at least 10 monomer units.
19. A polyolefin as claimed in claim 18 wherein said long chain branches are essentially homopolymeric.

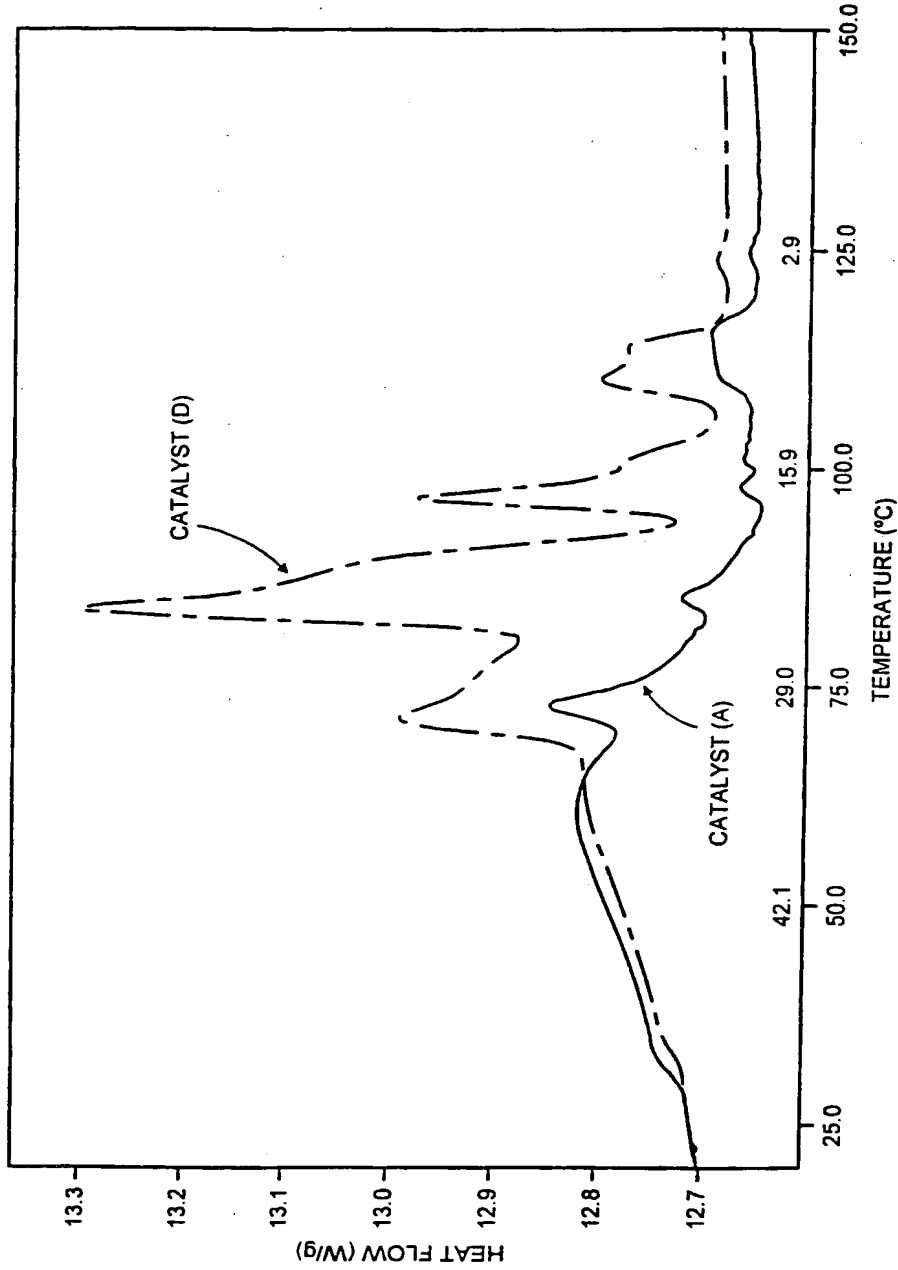


FIG. 1

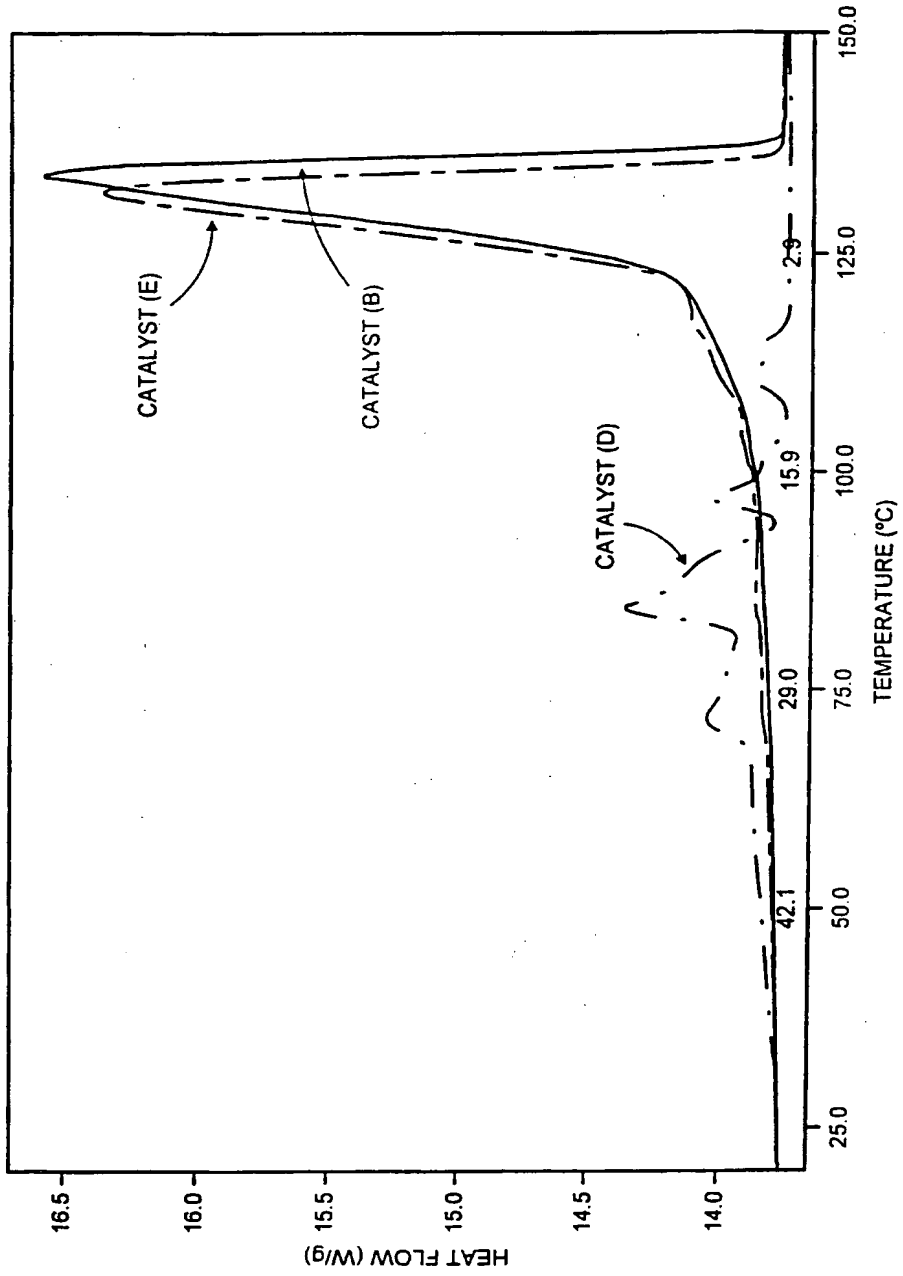


FIG. 2

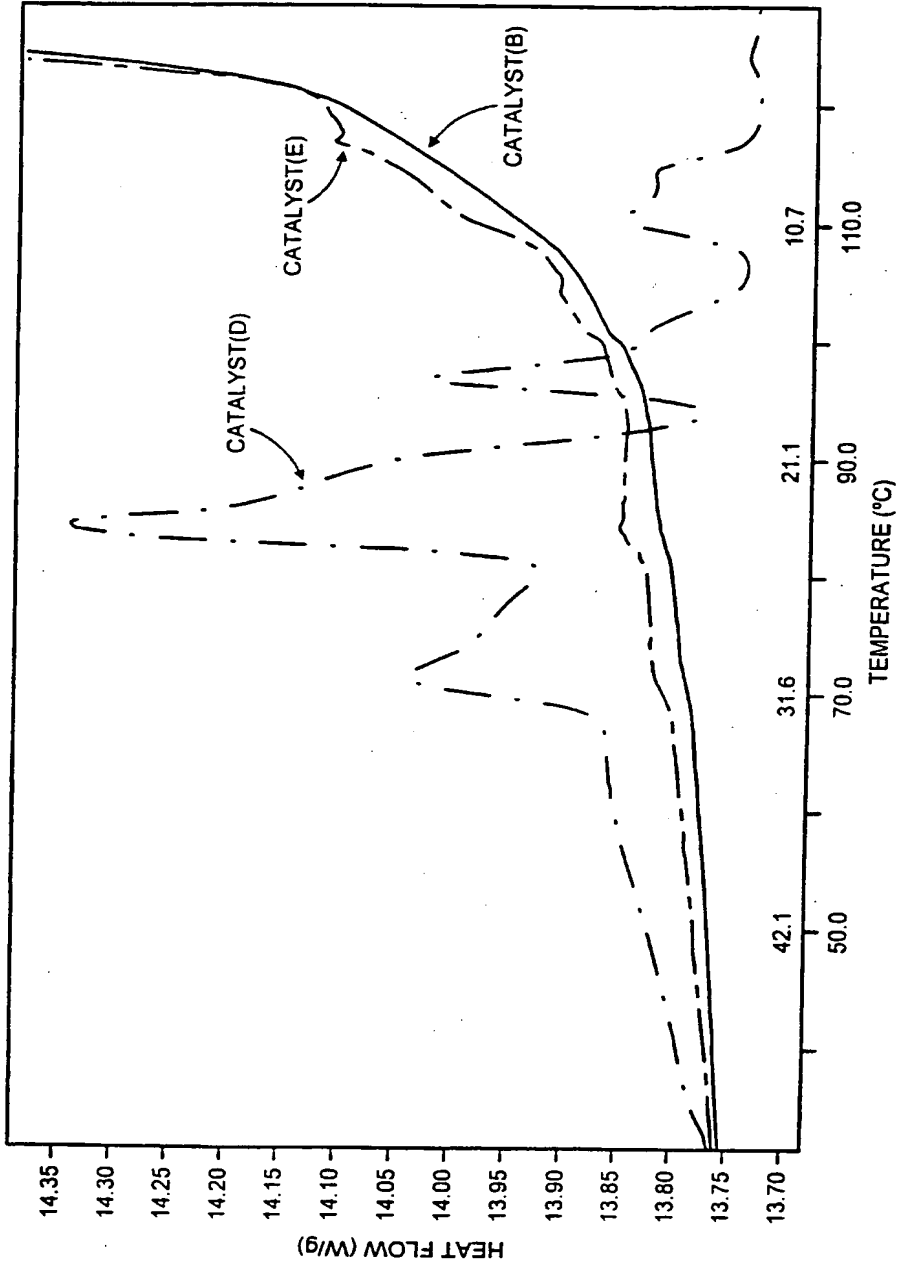


FIG. 3

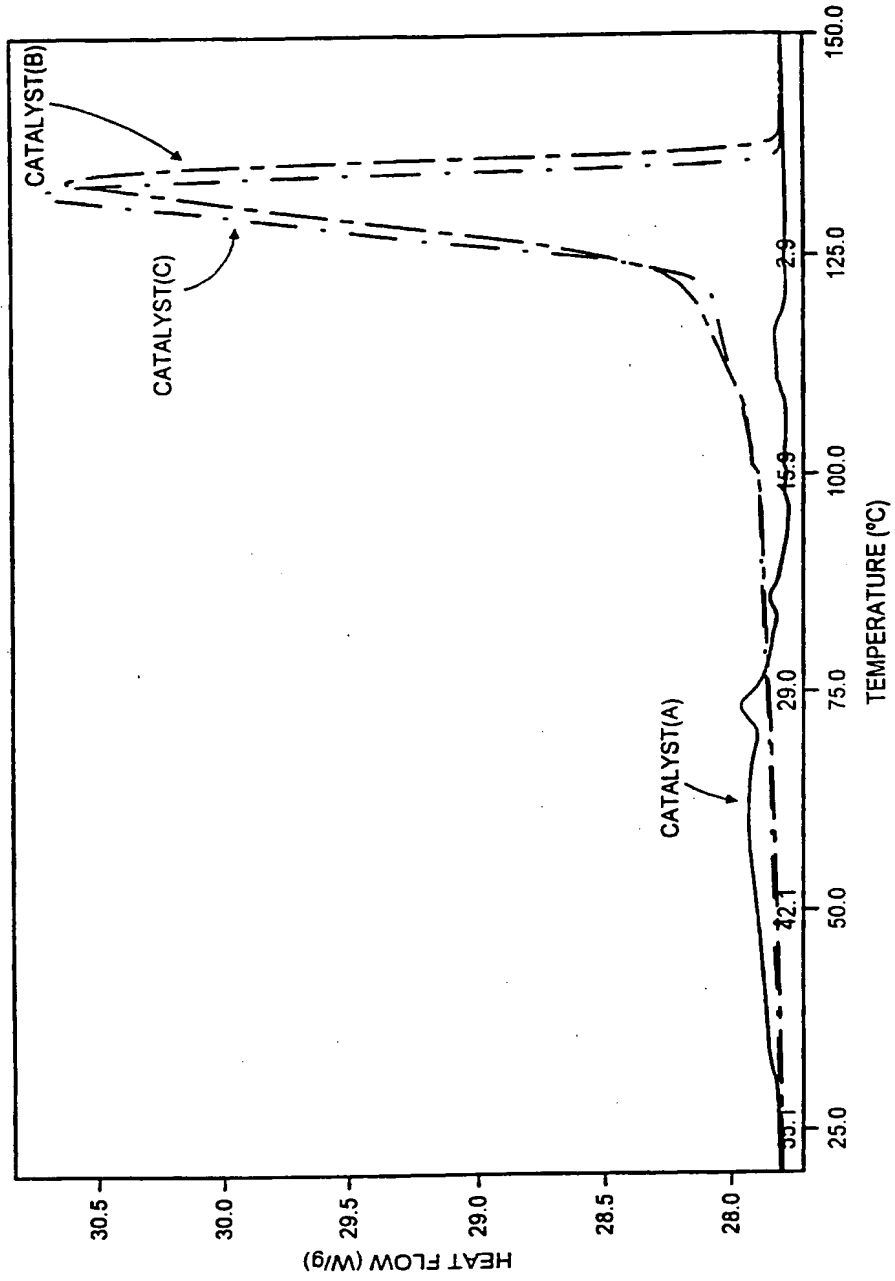


FIG. 4

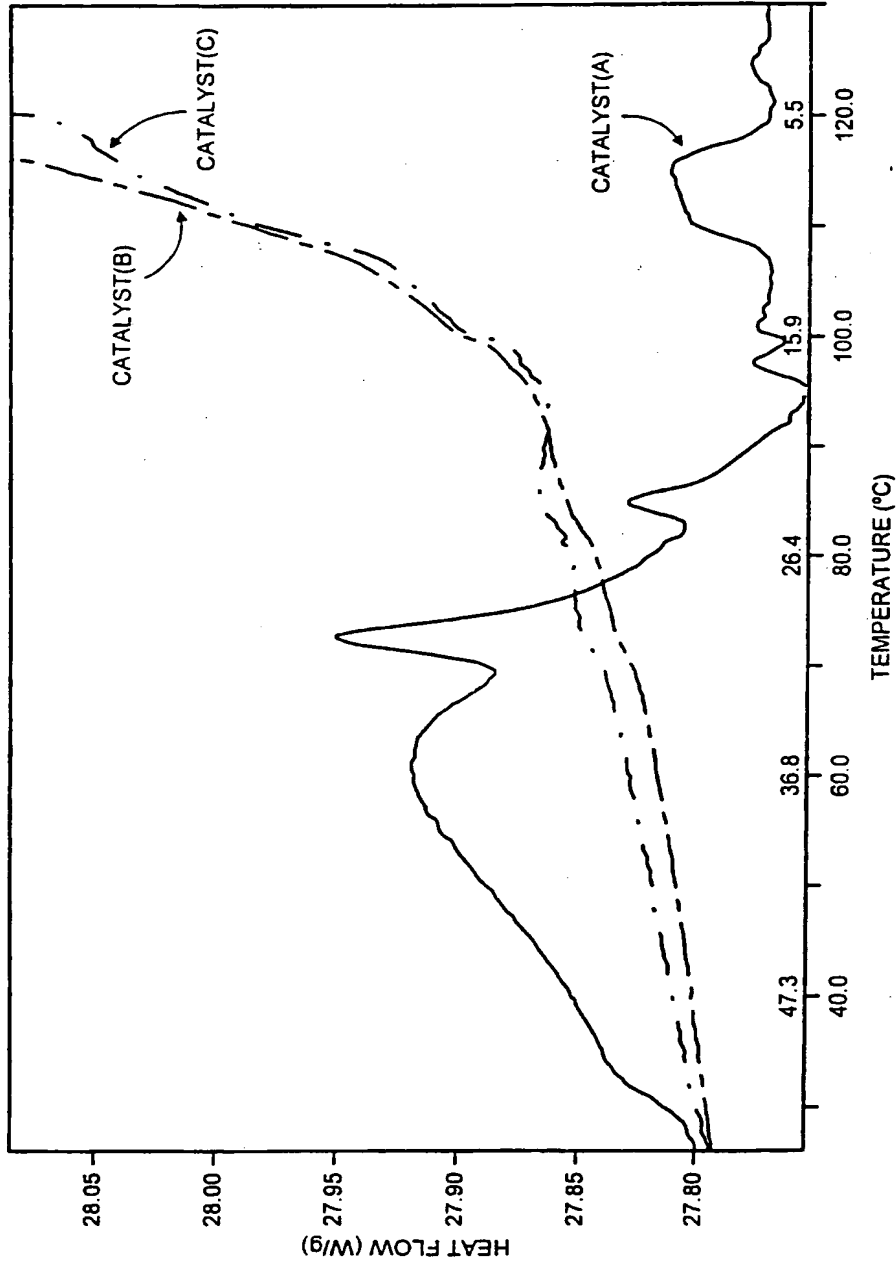


FIG. 5

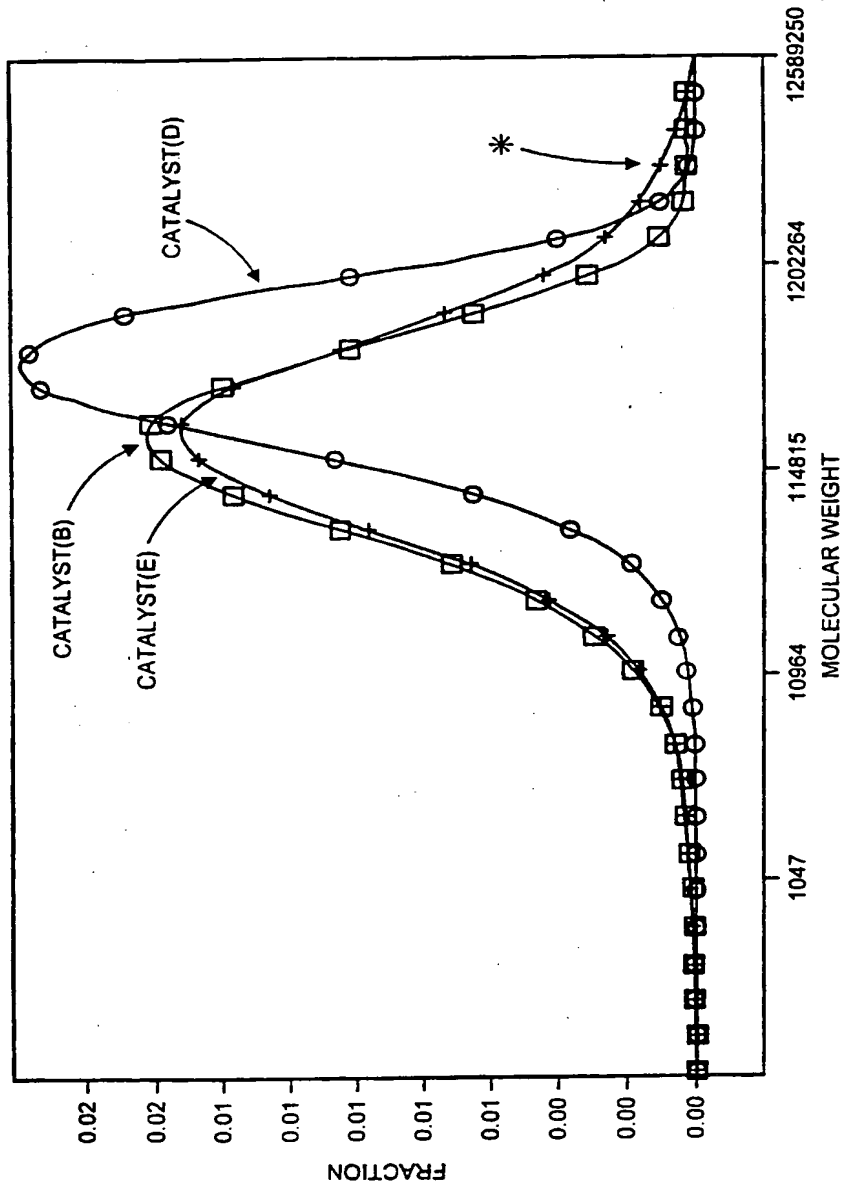


FIG. 6

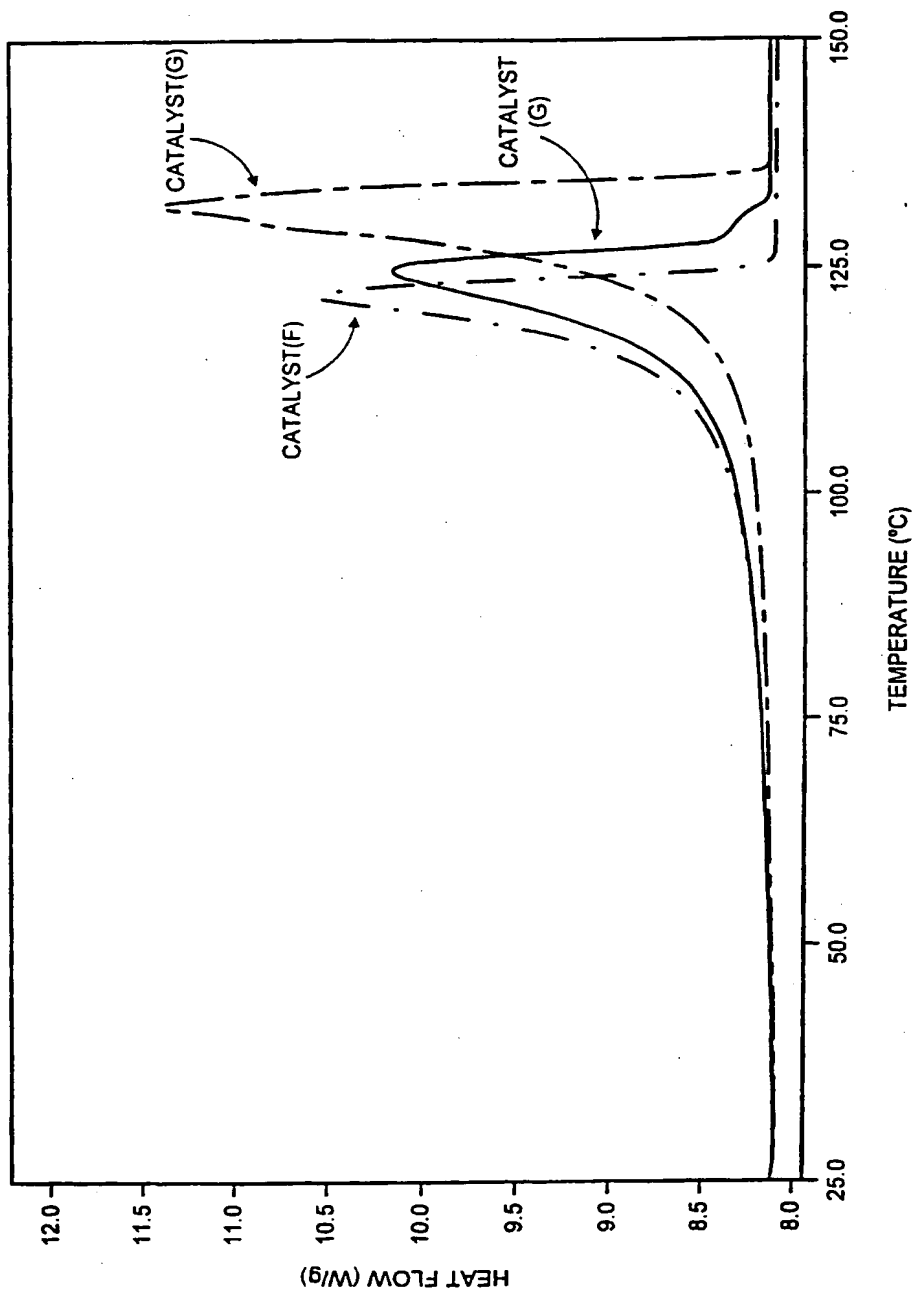


FIG. 7

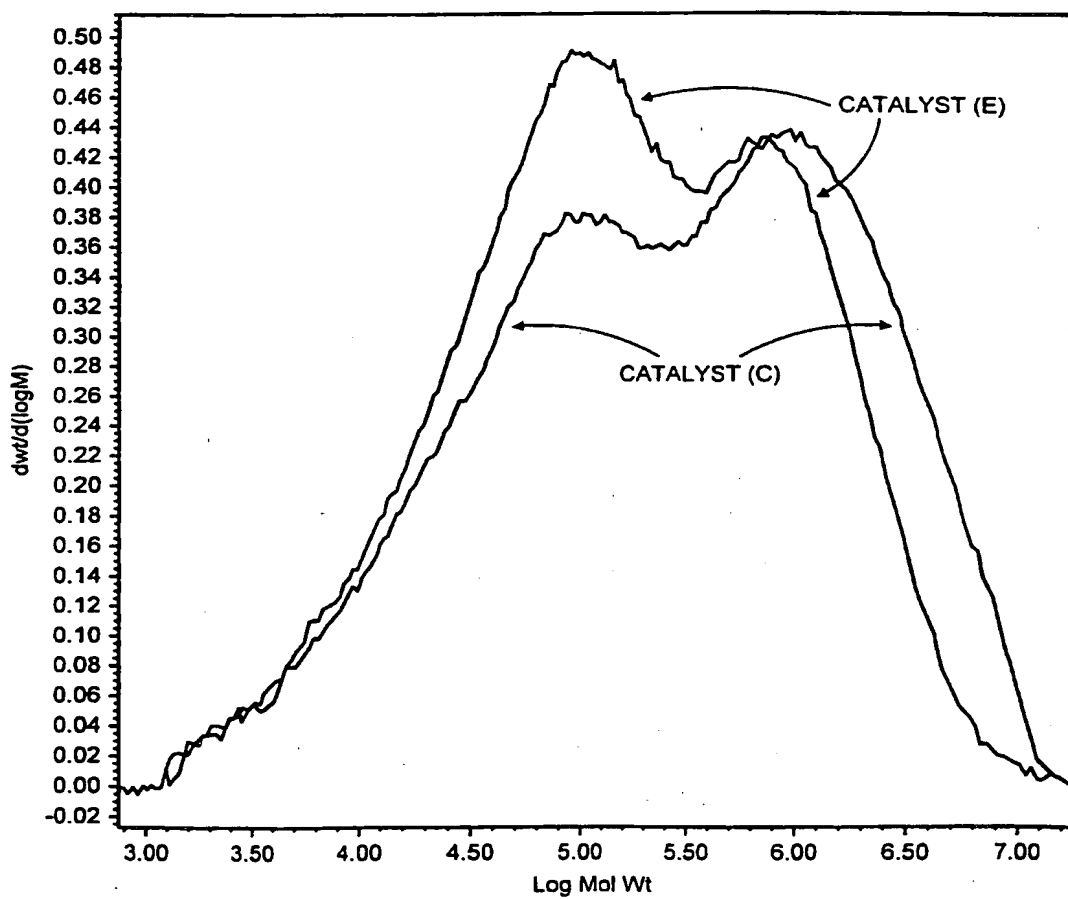


FIG.8

INTERNATIONAL SEARCH REPORT

International Application No
PCT/GB 00/02970

A. CLASSIFICATION OF SUBJECT MATTER IPC 7 C08F10/00 C08F4/642 C08L23/16				
According to international Patent Classification (IPC) or to both national classification and IPC				
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) IPC 7 C08F C08L				
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched				
Electronic data base consulted during the international search (name of data base and, where practical, search terms used) EPO-Internal, PAJ, WPI Data				
C. DOCUMENTS CONSIDERED TO BE RELEVANT				
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.		
X	WO 98 57998 A (BOREALIS AS ;COCKBAIN JULIAN (GB); NENSETH SVEIN (NO); FOLLESTAD A) 23 December 1998 (1998-12-23) cited in the application examples 3,4 ---	1,4-11		
X	WO 99 05153 A (TARGOR GMBH ;BINGEL CARSTEN (DE); FRAAIJE VOLKER (DE); KUEBER FRAN) 4 February 1999 (1999-02-04) examples 2,3 page 23, line 32 - line 44 page 24, line 13 - line 17 ---	1,4-11		
X	WO 97 43323 A (DUN JOZEF J VAN ;MIYAMOTO AKIRA (JP); MATSUSHITA FUMIO (JP); CHUM) 20 November 1997 (1997-11-20) page 114; example 9; table 3 page 116; example 13; table 5 ---	14,15		
-/--				
<input checked="" type="checkbox"/> Further documents are listed in the continuation of box C.				
<input checked="" type="checkbox"/> Patent family members are listed in annex.				
* Special categories of cited documents :				
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Date of the actual completion of the international search <p style="text-align: center;">30 November 2000</p>		Date of mailing of the international search report <p style="text-align: center;">11/12/2000</p>		
Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel: (+31-70) 340-2040, Tx. 31 651 epo nl. Fax: (+31-70) 340-3016		Authorized officer <p style="text-align: center;">Gamb, V</p>		

INTERNATIONAL SEARCH REPORT

International Application No
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